Subject: PCG thesis prize entry
Date: Monday, 31 January 2011 11:43
From: Anthony Phillips <aep40@cam.ac.uk>
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To: David Keen david.keen@stfc.ac.uk
Cc: david.allan@diamond.ac.uk, jmc61@cam.ac.uk

Dear Prof. Keen,

I am writing to submit my PhD thesis, "In situ X-ray characterisation of photoinduced structural changes in solid ruthenium-sulfur dioxide complexes", for the PCG's PANalytical Thesis Prize in Physical Crystallography. This thesis reports work done at the Cavendish Laboratory, Cambridge and was submitted on 2 November 2010; my degree was officially awarded on 22 January 2011. Rather than clog your inbox with a rather large file (15 MB) I have uploaded it to a web server: it can be downloaded at your convenience from

http://www.tcm.phy.cam.ac.uk/BIG/aep40/aephillips-thesis.pdf

Please let me know if you have any problems with this; if necessary I would be happy to provide the file by some other means.

I propose as referees Dr David Allan of Diamond Light Source (david.allan@diamond.ac.uk, +44 (0)1235 778644), who was the external examiner, and Dr Jacqui Cole of the Cavendish Laboratory (jmc61@cam.ac.uk, +44 (0)1223 337470), who was my research supervisor. Both have kindly agreed to comment on my work as required.

The thesis focuses on the nascent field of photocrystallography: the use of crystallographic techniques to probe structural changes in light-sensitive solids. In particular, I investigate photoinduced linkage isomerism in a family of ruthenium-sulfur dioxide complexes. This is an important topic in physical crystallography for three reasons. First, just as high-pressure studies provide access to a wealth of structures unknown under ambient conditions, photocrystallographic techniques also reveal structural features which are otherwise inaccessible. For instance, the OSO-Ru coordination mode is only achievable via photoexcitation. Second, in addition to the inherent interest of these new structures, materials that exhibit photoinduced structural changes often thereby have novel and useful physical properties. In particular, photoinduced linkage isomerism often causes photorefractive behaviour. For this reason, the materials I study are of interest for holographic data storage applications, which will have higher data storage densities and faster readout times than conventional optical media. Third and finally, the technique of photocrystallography is itself undergoing rapid development. Modern diffraction sources and detectors provide accurate and sensitive probes of photoinduced structural change, but the best techniques for extracting the maximum possible information from these data are still being explored. My thesis contributes a new analysis method to this discussion.

The key results of the thesis are presented in its four central chapters. First, the results of single-crystal photocrystallographic experiments, using both laboratory and synchrotron sources, on two new members of the Ru-SO2 family are presented. In both compounds, both side-bound and O-bound coordination can be photochemically induced; these results represent the first time O-bound coordination has been

observed at nitrogen temperatures. Second, I propose a "hybrid" method of data analysis to confirm that the data genuinely support the presence of the proposed photoinduced minority populations. This uses conventional least-squares refinement to fit the parameters of models with and without the photoexcited states; these models are then compared using techniques drawn from Bayesian statistics. This both confirms the experimental results presented here and adds a useful new technique to the arsenal of methods available for analysing crystallographic data. Third, I present DFT calculations which compare the photoinduced geometries actually observed to plausible isomers for which there is no experimental evidence. I show that the observed geometries are those with the least steric hindrance from the crystal surroundings. In the final core chapter, I present a XANES experiment, demonstrating that X-ray spectroscopy is also an effective means of probing photoexcitation in this family of materials, even where single crystals, or even crystalline powders, are not available.

I believe that this work constitutes a substantial contribution to the field of physical crystallography, and in particular photocrystallography, both by achieving significant new experimental and computational results and by demonstrating a novel method of analysing the data obtained. Thank you in advance for your consideration; I look forward to hearing from you.

Yours sincerely,

Anthony Phillips